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Molecular Dynamics\*

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## FRACTURE AND FLOW VIA NONEQUILIBRIUM MOLECULAR DYNAMICS[\*]

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### ABSTRACT

The scope of molecular dynamics problems designed to simulate materials properties is described, focussing on the limits computation imposes on space and time scales, as well as the limits theoretical understanding imposes on our knowledge of interatomic forces. Five strategies for improving the efficiency of the simulations are described. Shock-induced solid-solid phase transformations are discussed to illustrate these ideas.

### 1. SCOPE OF NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS

Experimental values of fracture toughness and yield strength vary over about six orders of magnitude. The corresponding laboratory fracture and plasticity experiments typically use specimens with dimensions measured in centimeters and deformation times ranging from a microsecond to a year. Computer experiments, designed to simulate laboratory experiments or to illustrate physical principles, although registering steady gains in size and duration, are far from being able to match these length and time scales. Molecular dynamics simulations have gained five orders of magnitude in complexity and speed since the Fermi-Pasta-Ulam calculations carried out at Los Alamos 30 years ago[1]. Presentday size and duration limits, which are now improving relatively slowly, sharply restrict the maximum scope of computer simulations of physical processes. The largest computer simulations have involved 161,604 particles[2] and the longest simulations correspond to physical times of order 1 microsecond.

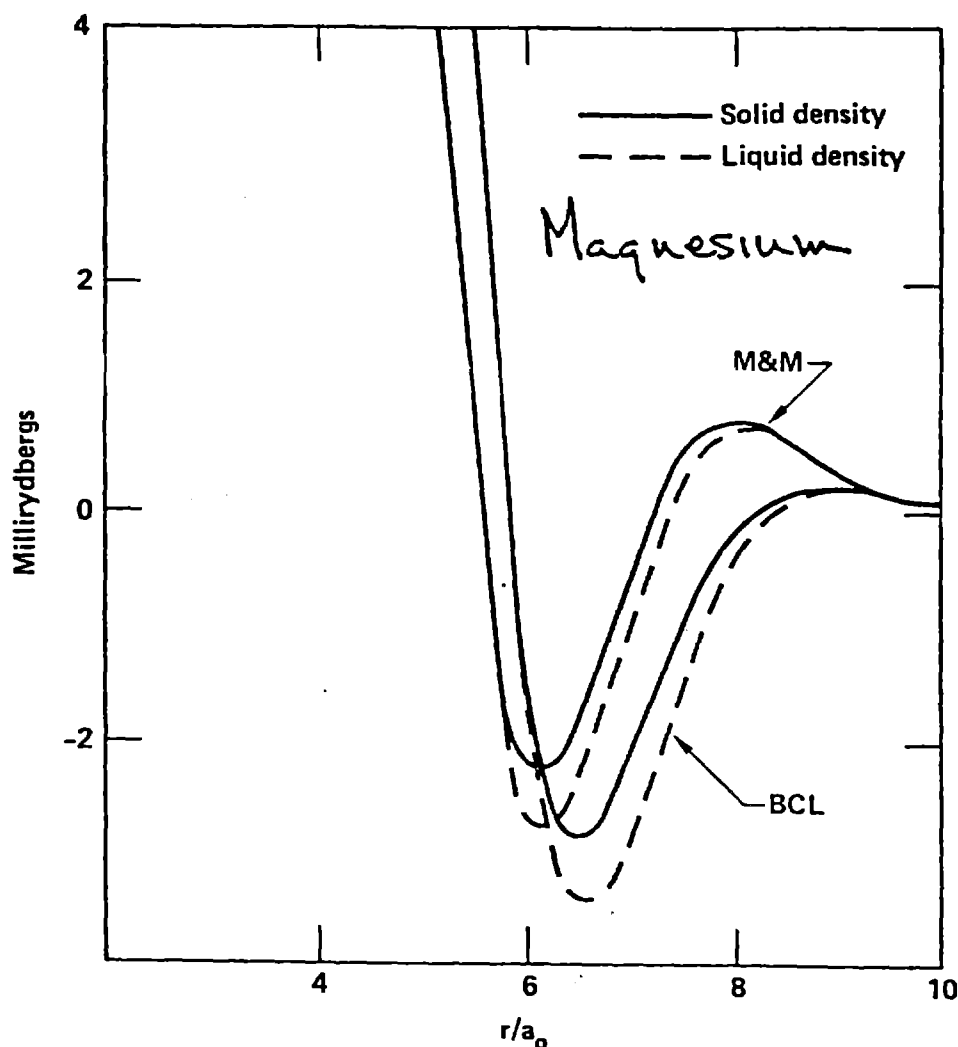
Both the laboratory-sized compact tension specimens used to measure fracture toughness and the Hopkinson-Bar specimens used to measure dynamic yield strengths, although "small," are still much too large for full-scale modelling at the atomistic level. Thus real laboratory creep experiments, in which metals flow very slowly under relatively small applied loads, are carried out with laboratory time scales ranging from seconds to years. The relatively much faster deformations caused by impacting small plastic sample disks with relatively-massive flying elastic bars, "Hopkinson-Bar experiments," with strain rates which can exceed 100,000 hertz, are still too slow for an accurate simulation of atomistic trajectories.

The computational limitations on space and time do not affect the accuracy of a simulation. Provided that we are satisfied with six-figure accuracy there is no difficulty in using Adams or Runge-Kutta finite-difference methods to integrate the equations of motion[3]. Despite this impressive numerical accuracy computer calculations can only be caricatures of the behavior of real materials. This is because our knowledge of interatomic forces remains primitive.

Current models[4,5] used for the interaction of relatively simple atoms, such as sodium and magnesium, are based on highly-intricate and detailed models for the electronic and nuclear structure of a metal. The complexity of this work defies exact description or reproducibility, and is a subtle mixture of art and science. Thus it is highly unlikely that a

typical published calculation incorporating these electronic pseudopotential models could be accurately reproduced, even with years of effort. The figure shows two recent versions of the effective atomic interaction in magnesium. The energy, in millirydbergs, is shown as a function of distance, in Bohr radii. The Moriarty-McMahan calculation[4] involves no adjustable parameters; the Barnett-Cleveland-Landman calculation[5] is fitted to experimental data. The difference between the two, around 15% at the potential minimum, gives a rough estimate as to the reliability of the theoretical work. Uncertainties of this order in the interaction potential are sufficient to shift the positions of phase transitions by pressures of order 10 kilobars and temperatures of order 100 kelvins.

The fact that density fluctuates rather wildly on an atomic scale suggests that no single density-dependent potential is likely to be a fully adequate approximation. In problems involving mechanical deformation one expects that energies of the order of microrydbergs could be significant. These energies, about six orders of magnitude below the hydrogen-atom energy, are three orders of magnitude smaller than the millirydberg scale of the figures. It seems highly unlikely that quantitative calculations of interactions will ever become possible on the accuracy scale necessary to reproduce mechanical behavior. The need for greatly improved accuracy in interatomic forces is well recognized. Serious efforts to calculate accurate atomic forces as functions of coordinates are underway. New emerging techniques may eventually make semiquantitative molecular dynamics possible[6], even for transition metals and covalently bonded materials.



## 2. STRATEGIES FOR EFFICIENCY IN MOLECULAR DYNAMICS

Molecular dynamics became possible with the development of computers for the weapons calculations of the second world war. The forces used in the early work were simple, slightly anharmonic springs or hard spheres with additional attractive forces, in keeping with the limits of knowledge and computational capacity. The original aim of molecular dynamics calculations was the understanding of a long-standing problem which fascinated Boltzmann and his colleagues, the consistency of Newton's reversible equations of motion with the irreversible second law of thermodynamics.

Fracture and flow, for instance, are irreversible processes. As a specimen is broken or caused to change shape, in an irreversible way, we nevertheless expect that the underlying dynamics is reversible, described either by Newton's or Schroedinger's equations of motion. It is a rare and unusual circumstance for a crack to heal, and the necked region of a tensile test specimen never reverts to its original diameter and shape if the tension is changed to compression. A detailed understanding of the paradox that reversible equations yield irreversible behavior was given by Boltzmann for dilute gases. Even so, this topic remains under intensive investigation 100 years later.

When the qualitative thermodynamic features of irreversibility and the existence of gas, liquid, and solid phases had been established, emphasis shifted to the cataloging of equilibrium and linear transport properties for more elaborate potentials. Inverse powers, combinations of powers, exponentials, and "realistic" pseudopotentials began to be studied. This work made it possible to assess the usefulness of the theories, developed in the period 1930-1960, which incorporated well-defined but poorly known distribution functions and made approximations of uncertain value. The computer experiments provided the first accurate distribution functions and were used to test the common truncation and superposition approximations of statistical mechanics.

In the past ten years the emphasis has changed, largely due to the success achieved by hard-sphere perturbation theory in calculating the thermodynamic properties for many-body fluid systems. A good survey of current research can be found in the proceedings of the 1985 Enrico Fermi Summer School on Molecular Dynamics Simulation of Statistical-Mechanical Systems. The present focus of attention has shifted to nonlinear dynamical problems such as those involved in fracture, plastic flow, and shockwaves[7]. The nonlinear work also makes contact with the current focus on the fractals and attractors associated with nonlinear dynamical systems[8].

During this past decade several strategies have been developed which have increased the power of molecular dynamics beyond what could be achieved by straightforward solution of Newton's conservative equations of motion. Here we list five strategies for such improvement:

1. Taking number-dependence of the microscopic results into account systematically in order to make more accurate macroscopic predictions.
2. Considering mesoscopic constitutive simulations with many degrees of freedom, intermediate between microscopic atomistic calculations and macroscopic continuum simulations.
3. Developing constrained dynamics so that independent variables other than energy and volume can be used. This work includes the introduction of

thermostats to remove irreversibly generated heat.

4. Developing corresponding states relationships, analogous to the scale models used in mechanical engineering, linking results for several related problems together.

5. Developing artificial processes to avoid at least a part of the size-dependence which makes full-scale simulation uneconomic.

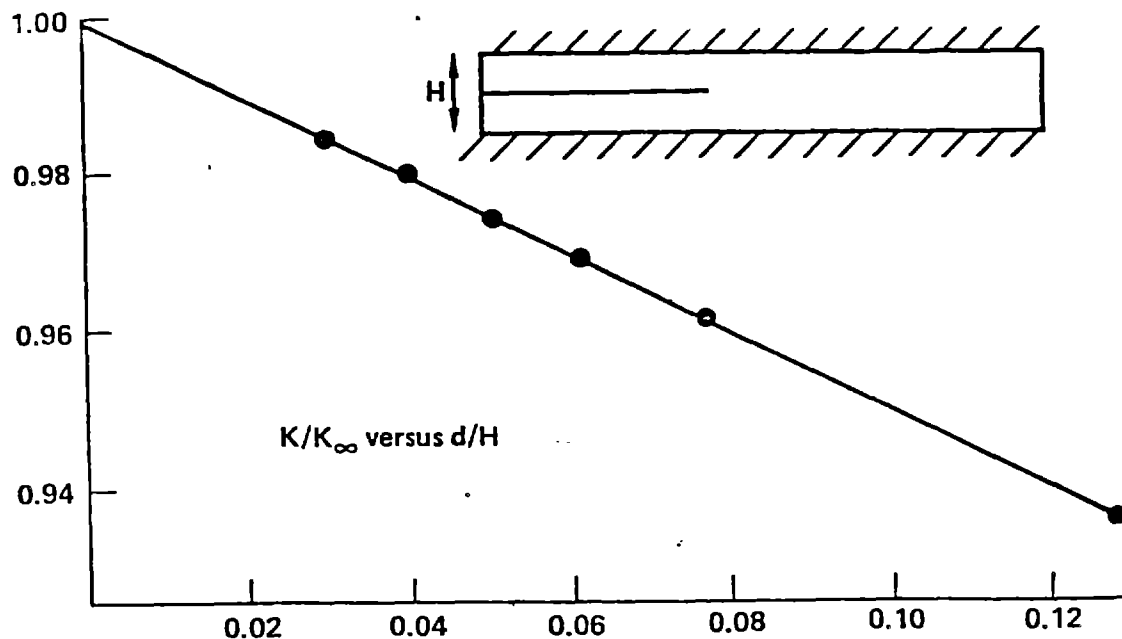
Let us consider these five strategies in more detail:

## 2.1 Number Dependence

Molecular dynamics is at its best in elucidating mechanisms on an atomic scale. Such mechanisms dominate problems involving fracture, plastic flow, or chemical reactions. Attempts to deal with these same problems using continuum mechanics are complicated by the presence of singularities in the continuum equations. The singularities in the stress and strain fields at cracks and dislocations are relatively long-ranged. The stress in the neighborhood of a crack tip in an elastic crystal falls off as the square root of  $L/r$ , where  $L$  is proportional to the size of the crystal.

The stress in the neighborhood of a dislocation also falls off slowly, as  $d/r$ , where  $d$  is the interatomic spacing. Thus simulations covering 1% of the sample size or 100 atomic diameters are required to reproduce, accurately, macroscopic stress fields in the vicinity of crystal defects.

The size dependence for many problems of interest in materials science is surprisingly straightforward to analyze. This is illustrated in the figure [9]. Stress near a brittle crack tip--made by cutting bonds linking the top and bottom halves of the crystals for 40% of the crystal length--was determined for a series of triangular-lattice two-dimensional crystals varying in size from 10 rows of 70 atoms to 40 rows of 280 atoms. The Hooke's-law linear force becomes increasingly attractive to a separation of  $1.15d$ , and then is reduced linearly to zero, vanishing at a cutoff of  $1.30d$ .



The top and bottom of the crystal were displaced in order to stress the crack, and the fracture toughness  $K$  was measured. The intercept from the empirical straight line shown in the figure is nicely consistent with the square-root dependence mentioned above. This correspondence of continuum and atomistic results on length scales large with respect to the range of interparticle forces makes it possible to combine these points of view in fracture and plasticity problems.

It is interesting to see that accurate data for crystals much too large for direct simulation can be obtained by extrapolating small-crystal data to the large crystal limit. This requires much less computer time than would a straightforward brute-force simulation of the stress field in the largest possible crystal. The results shown in the figure display much less size-dependence than would ductile cracks in crystals containing dislocations, or than would cracks in crystals with long-range, stiff interactions.

## 2.2 Mesoscopic Simulations

Lattice dislocations provide the mechanism for plastic flow. One part of a crystal flows relative to a contiguous part, through the motion of dislocations on the glide plane separating the two parts. The dislocations themselves can be treated as particles, in two dimensions, or as deformable lines in three dimensions. The dislocations move through a crystal with an equation of motion giving their velocity as a function of orientation and local stress. Dislocations can move at speeds near the sound speed under relatively small stresses. They interact with a tensor force and can react and combine to form other dislocations.

By studying the properties of dislocations, it has proved possible to determine equations of motion directly from computer experiments [10]. By including dislocation interactions and stress-induced motion, "mesoscopic" simulations of plastic flow can be carried out. Such simulations, intermediate in length scale between atomic and continuum calculations, greatly increase the potential of computer experiments in the understanding of plastic flow.

## 2.3 Thermostats

In any irreversible process, such as fracture or plastic flow, stored mechanical energy is converted to heat. The temperature in a "cold-worked" metal or in the vicinity of a propagating crack can exceed the ambient temperature by hundreds of kelvins. The fundamental source of this heat is the potential energy stored in the solid through the action of external deformation forces. The energy is released as heat in the irreversible process of breaking interatomic bonds. In laboratory experiments this heat can then be carried, by phonons, to the boundary of the system. A typical thermal diffusivity for a metal is one square centimeter per second. Thus, in a microsecond, heat diffuses about 40,000 particle diameters in a simple metal such as room-temperature sodium.

It is difficult to model this motion of heat on an atomistic level. This is because the phonons which carry the heat have free paths which often substantially exceed the size of convenient computational cells. Thus a third strategy for extending the capability of simulations is to introduce thermostats directly into the equations of motion. This eliminates the rapid changes of thermodynamic state which would otherwise accompany small-scale irreversible processes, and also makes it unnecessary to look at systems large with respect to a typical phonon mean free path.

Thermostats based on rescaling atomic velocities have been in use for over a decade. A recent breakthrough in this area was announced by Shuichi Nose[11,12], who found a way to obtain the canonical constant-temperature phase-space distribution from ordinary differential equations of motion slightly modified from Newton's equations:

$$ma = F - zmv,$$

where  $m$  is the atomic mass,  $v$ , and  $a$  are the velocity and acceleration,  $F$  is the force, and  $z$  is the friction coefficient. Nose calculated the friction coefficient as a memory function for the kinetic energy, proportional to the time integral of  $K - 3NkT/2$ .

The same friction-coefficient form of the equations of motion, including the linear thermostating force had already been used in simulations designed to keep the kinetic energy of selected sets of particles constant, but in the earlier work the friction coefficient had no memory. It was simply chosen to fix the kinetic energy (and has the form  $[dO/dt]/2K$ , where  $O$  and  $K$  are the potential and kinetic energies, respectively).

Several other forms of thermostats and ergostats have been introduced and compared[7,13]. So far each of these choices can be described, in the language of control theory, as differential, proportional, or integral control, but it seems likely that more general forms will emerge in the near future. The canonical Nose thermostat and the isokinetic Gaussian thermostat seem to be the most useful. Evans and Holian made a comparison of six different thermostats applied to the calculation of the nonlinear fluid viscosity. Although all six methods produced essentially the same viscosity the Gaussian thermostat was more efficient than the others by at least a factor of six in computer time[13]. Why it is that the nonlinear viscous response, far from equilibrium, is nearly independent of the type of thermostat used is not yet understood.

## 2.4 Corresponding States Relationships

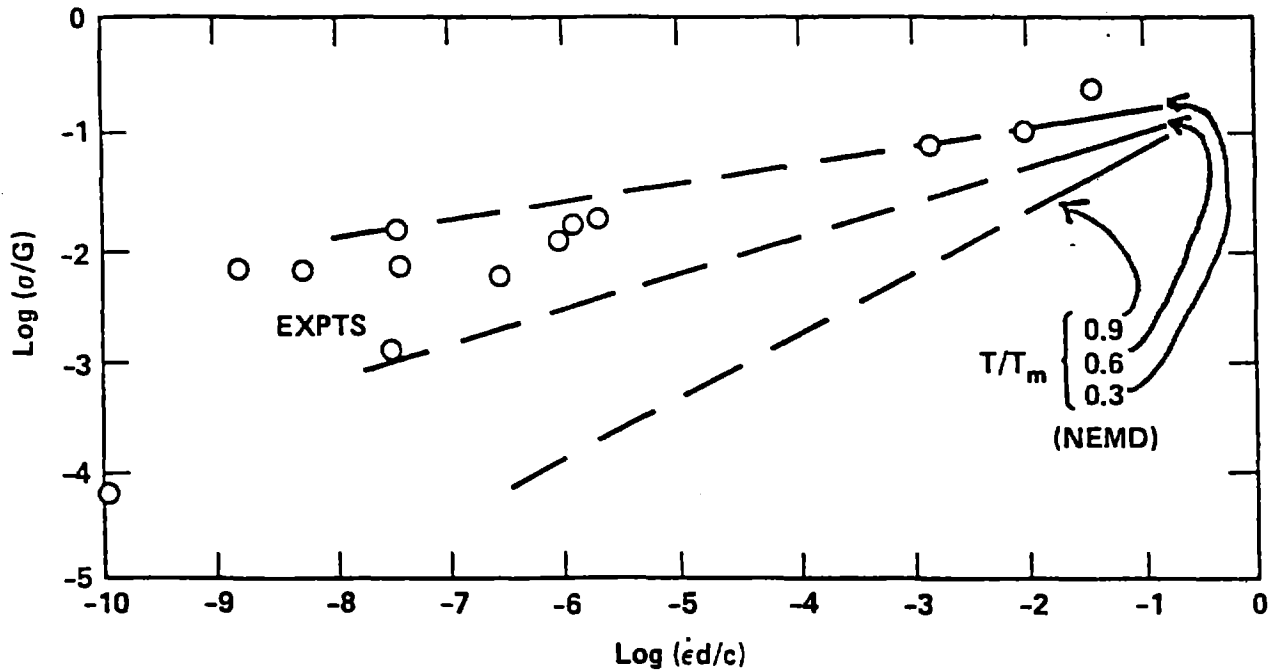
In metals the electronic energy is a sensitive function of density. Thus the corresponding pseudopotentials, such as those shown in the first figure, which impute a part of this energy to the ion cores, depend relatively strongly on density and nearby crystal defects. For this reason it may well be unrealistic in most cases, to imagine a quantitative simulation of a particular material. The many aluminum and iron alloys have very different fracture and flow properties relative to single crystals of the pure metals.

Thus corresponding states relationships which link together simulations with one structure or force law with other simulations can be extremely useful. These relationships identify properties which are insensitive to the form of interparticle forces and which therefore can be predicted, with fair confidence, from computer simulations. Van der Waals' fluid equation of state, which describes gas-liquid coexistence in a semiquantitative way, is a familiar example. By choosing characteristic van der Waals constants,  $a$  and  $b$ , many different materials can be described by the same equation of state.

Corresponding states relationships away from equilibrium are not so well known. At low rates of strain materials deform in individual ways, depending very much upon crystal structure, inclusions, grain size, radiation history, and a host of such variables. At high strain rates



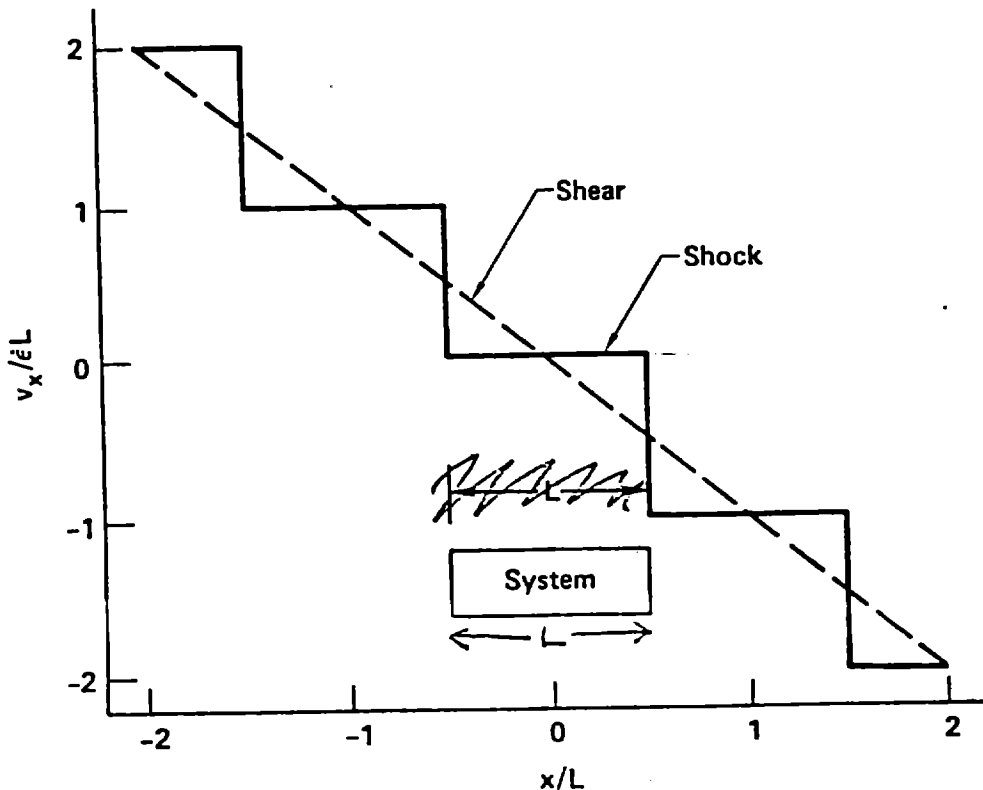
things become simpler. The figure shows the variation of solid-phase yield stress with strain rate for isothermal steady shear[14]. The stress is made dimensionless by dividing by the shear modulus. The strain rate is made dimensionless by using the interparticle spacing  $d$  and the transverse sound speed characteristic of dislocation motion. Within the width of the corresponding-states lines the two- and three-dimensional crystals produce the same results. An extrapolation of the computer data, the solid lines at the extreme upper right corner of the figure, agrees reasonably well with data, of uncertain validity, for metals. The temperatures of the computer simulations, relative to the melting temperature, are shown.



## 2.5 Artificial Processes

Finally, in some cases, it may be possible to replace inhomogeneous time-dependent physical processes by homogeneous artificial processes which span essentially the same thermodynamic states. This idea has been fully explored, for both fluids and solids, in simulating steady viscous flows and heat flows in fully periodic homogeneous systems[14,15].

Viscous flow has been simulated by using the dashed-line velocity field shown in the figure. The basic system extends initially from  $-L/2$  to  $L/2$ , and is repeated spatially with periodic boundaries. Then a macroscopic velocity, shown in the figure, is added to the initial microscopic thermal velocities. The smooth dashed line corresponds to simple longitudinal compression. If the macroscopic velocity varies in a series of steps, as shown with the heavy line, then a pair of shockwaves is generated, at  $-L/2$  and  $L/2$ . Shear flows, as well as flows combining shear and dilation can be simulated in an analogous way.

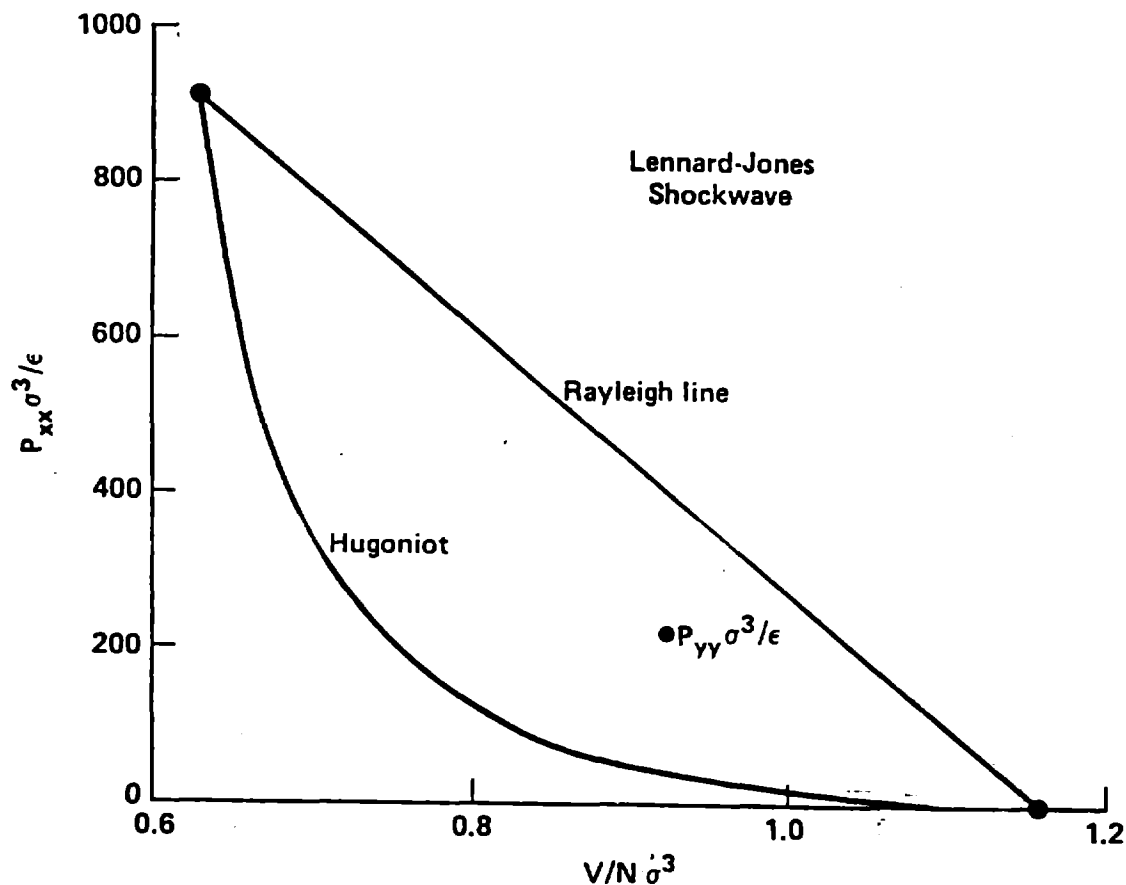


Heat flow has also been simulated in periodic homogeneous systems. This has been accomplished by using an external field, derived from linear response theory, which drives more-energetic particles in one direction and less-energetic particles in the opposite direction. It has to be emphasized that these artificial processes generating shear flows, shockwaves, and heat flows are not the same as those determined in laboratory experiments on the same thermodynamic state. But, as the Evans-Holian calculations[13] demonstrate, the differences are in most cases considerably less than the statistical uncertainties in the measured transport, and hence negligible. This potentially useful idea of artificially reproducing nonequilibrium states by using external forces is explored more fully in the last section. There we suggest a new method for simulating the polymorphic phase transformations induced by shockwaves.

### 3. SIMULATION OF SHOCK-INDUCED PHASE TRANSFORMATIONS

Shockwaves can produce high pressures[16] much more cheaply than static experiments and are therefore coming into relatively common use in materials research. Ongoing work at Livermore[17] is directed toward the low-cost shockwave-induced synthesis of superconductors from amorphous metals. The experiments proceed by treating relatively thin layers of metal with shockwaves of controlled pressure and duration.

The shock process is relatively complicated, even in the simplest steady-wave case. In this case, in a frame centered on the shock wave, the flows of mass, momentum, and energy are all constants. Otherwise, mass, momentum, or energy would build up in a part of the wave, which would then not be a steady one. The conservation equations for these three fluxes provide relations between the pressure tensor component in the shockwave direction, the density, and the heat flux. These state variables are connected in a definite way in a shockwave. As shown in the figure, the longitudinal pressure varies linearly with volume. The energy flux has a quadratic variation with volume.



How can these same states, characteristic of a steady shockwave, be traversed in molecular dynamics simulations in which homogeneous periodic boundaries are used? In the simulations we can follow the Gauss-Nose ideas of introducing a friction coefficient into the equations of motion. Because two constraints must be satisfied the shockwave-simulation friction coefficient is a tensor, with different components parallel and perpendicular to the shock propagation direction.

We are testing this idea in the one case where a strong dense-system shockwave transformation has been well characterized, the 400-kilobar shockwave studied by Holian, Hoover, Moran and Straub[18]. The main point which is presently unclear is the choice of strain rate which must be imposed on the simulation. When the fluid-phase results have been successfully reproduced we will apply the same idea to the solid transformations used to synthesize superconducting alloys. In the solid-phase shockwaves studied by Holian and Straub at Los Alamos considerable dependence of the shockwave structure on system width was found. Because the systems studied had to be many times longer than wide in order to study a steady profile, a cross section containing only 32 atoms was the maximum practical size. With the development of a new technique for homogeneous simulation of the shockwave process, cross sections containing a few hundred atoms should become possible.

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